

(19) Japanese Patent Office

(11) Publication Number
57-50912 (50912-1982)

(12) THE LAID-OPEN PATENT GAZETTE (A)

(51) Int.Cl.³ Identification Office File (43) Publication date 25th March 1982
Code Number

A 61 K 7/06 7432-4C

Number of Inventions 1

Request for Examination Not received

(Total 5 sheets)

(54) Title of the invention A composition for hair dressing

(21) Application number 55-127822 (127822-1980)

(22) Application date 12th September 1980

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Specification

1. Title of the Invention

A composition for hair dressing

2. Scope of Claim

1. A composition for hair dressing which is formed from a nonionic hydrophilic low-polymer (oligomer) which does not possess film-forming properties at room temperature, obtained by the polymerization or copolymerization of monomer containing at least 70 mol% of one or more than one type of acrylate or methacrylate monomer represented by the general formula



(where, in the formula, X is a hydrogen atom or a methyl group, and when Y is a hydrogen atom then n is in the range 1 to 10, when it is a methyl group then n is in the range 1 to 5, and when it is an ethyl group then n is in the range 1 to 3; furthermore, in the case where Y is a mixture of a hydrogen atom and/or methyl group and/or ethyl group, then n does not exceed 10 in the case when Y includes a hydrogen atom, and it does not exceed 5 when it includes a methyl group or ethyl group).

3. Detailed Description of the Invention

The present invention relates to a composition for hair dressing which shows a stable and effective hair dressing effect by incorporation primarily into hair dressing preparations.

In the cosmetics or toiletries (products for the bathroom or washroom) market, the materials referred to as hair dressing preparations include hair sprays, setting lotions, oily pomades, hair creams, liquid hair dressing agents (hair liquids), hair tonics, thickeners and hair treatments, and hair dressing effects (hair treatment effects) are also to be found in shampoos and rinses. As hair dressing components therein, there have been used for example natural or synthetic resins, oils/fats, waxes, surfactants, addition polymers of ethylene oxide/propylene oxide/butylene oxide on their own or as mixtures, and the phosphoric acid esters of these. However, due to recent changes in hair styles, in the case in particular of hair sprays and liquid hair dressing agents which are the most popular types of hair dressing preparation, there has been an increasing tendency to demand 'natural' hair dressing properties with a soft set.

Hitherto, in the case of hair sprays, those that provide 'hard-holding' have been valued and, as components with setting properties for this purpose, high-polymer materials which are alcohol-soluble and have hair washability, and which are soluble in aerosol propellants and have a moisture-resistant film-forming capacity, such as shellac, polyvinyl pyrrolidone, polyvinyl pyrrolidone/vinyl acetate copolymer, vinyl methyl ether/partially-esterified maleic anhydride copolymer, vinyl acetate/crotonic acid copolymer, acrylic acid esters, methacrylic acid ester copolymers and the like, have normally been used. However, these all form hard films so, at the time of hair dressing, the set is 'hard' and it is difficult to obtain a

'natural' hair shape. Attempts have been made to deal with this by synthesizing polymers where the film formed is soft, and by the incorporation of additives such as plasticizers, oils/fats, silicone oils and the like. However, such methods either have hardly any effect or, by increasing the viscosity, they actually produce a heavier set, a non-dry touch, flaking, soiling and poor combing, and the effects of a softer set cannot really be achieved. Again, there are formulations where the amount of resin component incorporated is suppressed and while these do show some degree of effect depending on the mode of use, they are not a fundamental solution to the problem.

Furthermore, in the case of liquid hair dressing agents, hitherto there have primarily been used propylene oxide adducts of butyl alcohol or the phosphoric acid esters thereof, but the propylene oxide adducts of butyl alcohol give the hair dressing properties an oily feel (the hair hangs in a 'clammy' fashion), and they are unsatisfactory in their setting and hair washing properties. Moreover, when included in a liquid hair dressing formulation, only alcohol can be used as the solvent. On the other hand, while the phosphoric acid esters of butyl alcohol propylene oxide adducts are somewhat improved in terms of such oiliness and unsatisfactory setting and hair washing properties, their set is 'heavy' and they give the impression of not being clean. Furthermore, the esterified phosphoric acid derivatives are neutralized with a basic material in order to provide water solubility and to adjust the pH, etc, so maintaining uniform properties is complex.

In the case of shampoos and rinses, recently, for the purposes of foam stability and improving the feel at the time of shampooing or rinsing, or again for improving the feel after washing and to improve the hair treatment properties, examples have been seen where these effects are manifested by incorporating oils/fats, surfactants and resins which are slightly adsorbed onto the hair and have a slight foam stabilizing effect. For example, besides the acrylate type anionic resins, polypeptides, lanolin-based surfactants and the like used in hair sprays, there have been incorporated into products such as shampoos and rinses about 0.1 to 1% of nonionic phosphate ester or phosphate ester salt of a butyl alcohol adduct with ethylene oxide, propylene oxide, butylene oxide or mixture thereof. In the case of the compositions relating to the present invention described below, use for the same objectives is possible. In particular, the compositions relating to the present invention are nonionic so there is the advantage that formulation can be carried out safely and stably in any proportions in shampoos (primarily anionic surfactants) and rinses (primarily cationic surfactants).

To meet the demands of the market as described above, the present inventors have carried out painstaking research based on the idea that, by using a hydrophilic nonionic low-polymer (oligomer) without film-forming properties, comprising an acrylic or vinyl starting material, it would be possible to meet these demands. As a result, they have obtained the composition of the present invention.

The present invention has the objective of providing novel hair dressing preparations using, as the hair

dressing preparation or as a base or additive for a hair treatment agent, a hair dressing composition comprising a nonionic hydrophilic low-polymer (oligomer) which does not possess film-forming properties at room temperature, obtained by the polymerization or copolymerization of monomer containing at least 70 mol% of one or more than one type of acrylate or methacrylate monomer represented by the general formula



(where, in the formula, X is a hydrogen atom or a methyl group, and when Y is a hydrogen atom then n is in the range 1 to 10, when it is a methyl group then n is in the range 1 to 5, and when it is an ethyl group then n is in the range 1 to 3; furthermore, in the case where Y is a mixture of a hydrogen atom and/or methyl group and/or an ethyl group, then n does not exceed 10 when Y includes a hydrogen atom, and it does not exceed 5 when it includes a methyl group or ethyl group).

As examples of the polymerizable materials used in practising the present invention, there may be considered the acrylic acid and methacrylic acid esters of ethylene glycol, propylene glycol, butylene glycol, polyethylene glycol (number of added mols up to 10)ⁱ, polypropylene glycol (number of added mols up to 5) or polybutylene glycol (number of mols added up to 3) and, in terms of stable addition to formulations as a hair dressing agent additive, it is necessary that they be non-ionic monomers. With the molecular weight being low, there will be sufficient adhesion to the hair and, according to the formulation and properties of the target hair dressing preparation, the polymerization is

carried out using a mixture with other copolymerizable component(s) in which the aforesaid monomer component is adjusted to comprise 70 to 100 mol%. In the case where used as a hair spray or liquid hair dressing agent, the amount incorporated will be comparatively large and it is necessary to give adequate attention to the hair washing properties. Either a comparatively large proportion of the aforesaid monomer component is incorporated or there is primarily used monomer where Y in the above general formula is a hydrogen atom, that is to say a polyethylene glycol type monomer. On the other hand, in the case when incorporated into a shampoo or rinse agent, a certain amount of adsorption onto the hair, foam stabilization and feel are important, so the aforesaid monomer component is reduced down to 70 mol% and water solubility and moisture absorption are lowered. Now, if the amount is reduced to below 70 mol%, the residue on the hair will be increased and there is a sticky sense after washing, so that a pleasant feel is not produced. In obtaining the composition relating to the present invention, as examples of copolymerizable monomers other than the aforesaid monomer components, there are the aliphatic alcohol esters of acrylic acid and methacrylic acid, vinyl acetate, vinyl propionate, acrylamide, N-methylol acrylamide, N-butoxyacrylamide, dimethyl acrylamide, diacetone acrylamide and the like.

Next, the problems arising when the monomer represented by the above general formula is less than 70 mol% will be described in detail for various types of hair dressing preparation. Firstly, in the case of a hair spray, the fact that when the water solubility is insufficient the hair washing properties become poor has

already been mentioned, but in addition the 'spread' of the sprayed material on the hair and the levelling properties are inadequate, so a shine does not readily appear. Furthermore, there is separation and cloudiness on hair which contains moisture and so the 'set' is unattractive. In the case of a liquid hair dressing preparation, it becomes impossible to replace the ethanol in the product solvent with water, so there is no product cost reduction, no mitigation of the removal of oils from the hair and scalp at the time of use, and no lessening of the danger of catching fire. Moreover, when incorporated into a shampoo or rinse, since the amount of residue becomes too great and there is a slippery feel to the touch due to the increased oiliness, there is matting of the hair and combing is unpleasant.

The major characteristic of the composition relating to the present invention is that it is nonionic. That is to say, most of the aforesaid conventional hair dressing preparations are anionic, and these are mostly neutralized with amines to provide water solubility for use as a hair dressing preparation. However, as a result of this neutralization the pH is weakly alkaline, which has undesirable effects on the hair. Furthermore, it is a cause of discoloration and may produce an unpleasant smell such as the smell of the amine. Now, hair dressing resins which have been made amphoteric or cationic are also to be found but they have problems such as being sticky, having a smell, or giving washing difficulties with anionic shampoos. While conventional polypropylene glycol type compounds used as liquid hair dressing materials are nonionic, they suffer from

problems in that they are not hydrophilic, they are sticky and they have poor hair washing properties.

In contrast, a major feature of the hair dressing composition of the present invention is that it is both nonionic and, furthermore, hydrophilic. In the general formula



when Y is a methyl group then n is 1 to 5, and when it is an ethyl group then n has to be 1 to 3. These are necessary conditions for the composition of the present invention to be nonionic and, furthermore, to be hydrophilic. If n is greater than the stated figure, the hydrophilic character is insufficient and the material is undesirable in practical terms. Now, when Y is a hydrogen atom, then even when n is 11 or more there is no change in the water solubility but the material becomes crystalline, so that it is no longer desirable as a hair dressing material. Again, consideration can also be given to the case where Y is a mixture of hydrogen atom, methyl group and ethyl group, that is to say the case of addition copolymers of ethylene oxide, propylene oxide and butylene oxide, and here too the same applies. That is to say, there can be used such monomer to form the composition relating to the present invention providing it falls within the range of being hydrophilic and non-crystalline.

At the time of the polymerization, where required it may be useful to employ the usual molecular weight regulating agents. The polymerization conditions will differ according to the desired properties and the

monomer composition but in order to efficiently produce material with as low a molecular weight as possible, there is used, as the polymerization solvent, a solvent having an alcoholic hydroxyl group such as an alcohol with an alkyl group like ethyl, propyl, butyl, amyl, hexyl or octyl, an ether alcohol such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, 3-methyl-3-methoxybutanol or 3-methoxybutanol, or an ester of an organic acid such as methyl lactate, ethyl lactate, propyl lactate, butyl lactate, amyl lactate, methyl citrate, ethyl citrate, methyl malate or ethyl malate, or there may be used 1,1-trichloroethane, perchloroethylene or the like. As the initiator used in the polymerization reaction, it is preferred that there be used an initiator which decomposes at a comparatively high temperature, such as cumene hydroperoxide (decomposition temperature 159°C), diisopropylbenzene hydroperoxide (150°C), di-tert-butyl peroxide (126°C), 1,3-bis-(tert-butylperoxyisopropyl)benzene (127°C), tert-butyl perbenzoate (105°C), or the generally-used benzoyl peroxide, lauroyl peroxide or the like.

The polymerization reaction is carried out using a polymerization reaction autoclave equipped with an ordinary stirring means, reflux condenser, thermometer, monomer dropwise addition device and nitrogen gas inlet tube, and after thoroughly purging the reactor interior and solvent with nitrogen gas, polymerization is carried out while continuing to introduce nitrogen gas. Following the dropwise addition of the monomer, a period of maturation is employed so that the polymerization

reaction is taken to completion, after which the solvent is recovered and purification, etc, carried out, to produce the hair dressing preparation starting material.

Below, examples of the present invention are provided.

[Example 1]

117 g of ethylene glycol monobutyl ether and 16.4 g of tert-butyl perbenzoate (decomposition temperature 105°C) were introduced into a flask of 1 litre capacity provided with a thermometer, stirring means, reflux condenser, monomer dropwise addition device and nitrogen gas inlet tube, and after passing nitrogen gas through the gas inlet tube for 10 minutes, the temperature was held at 130°C and, from above, there was added dropwise over a period of 3 hours, using the dropwise addition device, a mixture of 104.4 g (90 mol%) of 2-hydroxyethyl acrylate and 12.8 g (10 mol%) of butyl acrylate. Following the completion of the dropwise addition, there was added four times, at 30 minute intervals, 1 g of tert-butyl perbenzoate dissolved in 10 g of ethylene glycol monobutyl ether. Subsequently, the mixture was kept for 3 hours at 130-150°C, so that complete reaction was achieved. Thereafter, the solvent was distilled off under reduced pressure and adjustment performed by the addition of ethyl alcohol so that the resin component comprised 50%. There was obtained a hair dressing composition of product viscosity 25 centistokes (25°C).

20 g of this hair dressing composition was taken, then 80 g of ethyl alcohol added and 0.5 g of fragrance also added, to produce a base liquid. 80 g of this base liquid was sealed in an aerosol container of internal

capacity 220 ml and, to this, there was suitably added a mixed propellant gas of 48 g of trichloromonofluoromethane and 72 g of dichlorodifluoromethane, to produce a soft-type aerosol hair spray. When the hair spray obtained was applied to the hair, there was absolutely no tackiness or clamminess, a natural hair style was conferred and, in addition, sufficient setting strength was obtained.

[Example 2]

200 g of ethyl lactate and 26.5 g of 1,3-bis-(tert-butyl peroxyisopropyl)benzene (decomposition temperature 127°C) were introduced into the same equipment as in Example 1. After introducing nitrogen gas for 10 minutes through the gas inlet tube, the internal temperature was held at 150°C and, from above, there was uniformly added dropwise over a period of 3 hours, using the monomer dropwise addition device, 258 g (100 mol%) of hydroxypropyl acrylate. Following the completion of the dropwise addition, there was added four times, at 30 minute intervals, 2.6 g of 1,3-bis-(tert-butylperoxyisopropyl)benzene dissolved in 20 g of ethyl lactate. Subsequently, the mixture was held for 3 hours at 150°C, to take the reaction to completion. Thereafter, the solvent was distilled off under reduced pressure and adjustment performed by the addition of ethyl alcohol so that the resin component comprised 50%. There was obtained a hair dressing composition of product viscosity 45 centistokes (25°C).

42.5 g of purified water and 12.5 g of ethyl alcohol were added to 30 g of this hair dressing composition, and 1.5 g of fragrance also added, to produce a liquid

hair dressing agent. The liquid hair dressing agent thus obtained contained considerable water in the solvent but it was perfectly transparent and, when applied to the hair, there was a sense of slipperiness from the alcohol solvent and the set was extremely soft and showed a 'natural' finish.

[Example 3]

Using the same equipment as in Example 1, 100 g of tributyl citrate ester (Citroflex, made by Pfizer) and 10 g of diisopropylbenzene hydroperoxide (decomposition temperature 150°C) were added and, after introducing nitrogen gas for 10 minutes through the gas inlet tube, the temperature was held at 180°C. From above, there was uniformly added dropwise over a period of 3 hours, using the monomer dropwise addition device, a mixture of 108 g (70 mol%) of an ethylene oxide adduct (9 mols of added ethylene oxide) of methacrylic acid and 19 g (30 mol%) of dodecyl methacrylate. Following the completion of the dropwise addition, there was added four times, at 30 minute intervals, 1 g of diisopropylbenzene hydroperoxide dissolved in 10 g of butyl lactate. Subsequently, the mixture was kept for 3 hours at 180°C, to take the reaction to completion. Thereafter, under reduced pressure the 40 g of butyl lactate was recovered and there was obtained a hair dressing composition of product viscosity 170 centistokes (25°C).

A clear shampoo was produced using 2 g of the hair dressing composition thus obtained, 16 g of sodium alkyl ether sulphate, 4 g of lauric acid diethanolamide, 2 g of propylene glycol, 0.7 g of fragrance and 75.3 g of

water. When used on the hair, there were no untidy tufts of hair and the hair hung well.

Furthermore, as an oil rinse, 39.15 g of water was added to 2 g of stearyl trimethyl ammonium chloride, 1.5 g of polyoxyethylene cetyl ether, 5 g of propylene glycol, 0.1 g of citric acid, 0.15 g of sodium citrate, 0.1 g of methyl p-hydroxybenzoate and 2 g of the aforesaid hair dressing composition, to produce a rinse agent, and when a rinse treatment was carried out following shampooing, a good hair dressing treatment effect was seen.

Agent

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